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ADHESIVE COMPOSITIONS

The present invention relates to adhesive compositions.

5 There has been considerable interest in the general field of adhesives for use in the rapid mass-production of a wide range of products. However, adhesive bonding, particularly with known high-strength durable adhesives, has been relatively slow and/or has required special equipment.

10 Acrylic-based adhesives, cured by free-radical addition reaction mechanisms, have been suggested for use in applications which require fast curing and flexible adhesive composition. While these acrylic-based adhesives form flexible bonded joints which exhibit
15 beneficial properties in some applications, they often possess unacceptable water, solvent, and heat-resistant qualities.

Curable epoxy resins have also been used as adhesive compositions. By contrast to the free-radical
20 addition-curing catalysts which are used with acrylic-based adhesives, the epoxy resins are polymerised by ionic addition mechanisms and often require high curing temperatures and long setting times. While epoxy adhesives form a tight polymer network and are
25 characterised by durability, good adhesion, and good water, chemical, and heat-resistant qualities, they tend to be brittle, and their long curing times render them inappropriate for many industrial applications.

It is generally recognised in the art that
30 acrylic-based adhesives and epoxy resin-based adhesives are mutually non-reactive. For example, US-A-3684617 discloses an adhesive mixture of acrylic-based monomer and epoxy resin, each of which requires its own curing agent, resulting in separate curings without
35 interbonding. Moreover, mixtures containing an epoxy

resin component which does not react are disclosed in, for example, US-A-3994764, in which an epoxy resin is selectively added to an acrylic-based adhesive.

5 A polymerisable composition according to the present invention comprises 1 part by weight of a polymerisable epoxide-based material; no more than 1.8 parts by weight of a polymerisable acrylic-based material; and a bifunctional compound; in which the polymerisable materials are mutually substantially non-reactive at
10 ambient temperature, and in which the bifunctional compound can react with both polymerisable materials at ambient temperature; and in which the composition additionally comprises a catalyst and a catalyst initiator. The present invention utilises, and combines,
15 the unique properties of acrylic-based and epoxide-based materials.

GB-A-2110705 discloses and claims a polymerisable composition which comprises 1 part by weight of a polymerisable epoxide-based material; no more than 1.8
20 parts by weight of a polymerisable difunctional acrylic-based material; and a bifunctional compound as defined above.

As used herein, the term "acrylic-based" adhesive material is used generically and generally refers to the
25 chemical structure $\text{CH}_2=\text{CR}_1-\text{COO}-$, wherein R_1 can be hydrogen, methyl or ethyl. The material can be an acid, e.g. acrylic acid, or an ester, e.g. methyl methacrylate. As is known in the art, polymerisation of such materials proceeds by a free-radical addition polymerisation
30 mechanism, when a free-radical initiator interacts with the carbon-carbon double bond.

As used herein "epoxy resins" are compounds containing the three-member epoxide group (or ring). The simplest compound of this type is ethylene oxide, where
35 the two carbon atoms of the ring are bonded to hydrogen,

but generally they are bonded to more complex, organic, e.g. aliphatic, cyclic or aromatic (or any combination) backbones. It is known in the art that epoxide groups react via ionic addition mechanisms.

5 The bifunctional compound which is used herein has two chemically-reactive groups of different functionality. One functional group is epoxide-based chemically-reactive and the other functional group is acrylic-based chemically-reactive. Examples of suitable
10 bifunctional compounds are glycidyl methacrylate and methacrylic acid.

 "Bifunctional", as used herein, should be distinguished from "difunctional"; difunctional compounds have two chemically-reactive groups of the same
15 functionality. Examples of difunctional compounds are ethoxylated bisphenol A dimethacrylate and bisphenol A diepoxide.

 It is often preferred that bisphenol A (also known as 4,4'-isopropylidenediphenol) should be the chemical
20 backbone of the difunctional molecule, although a variety of other suitable chemical structures can be used. A typical diepoxide adhesive component used in the present invention is the diglycidyl ether of bisphenol A; and a typical diacrylic-based adhesive component used is
25 ethoxylated bisphenol A dimethacrylate. These two examples of difunctional molecules are structurally similar but chemically very different.

 It is known that acrylic-based adhesives usually require the presence of a catalyst of the free-radical
30 type. Known such catalysts include the organic peroxides, organic hydroperoxides, and organic peresters, which can be exemplified respectively by benzoyl peroxide, cumene hydroperoxide and acetyl peroxide. It is known in the art that acrylic-based materials

generally contain inhibitors. It is also known in the art that other materials can also be added to the acrylic-based adhesive composition to affect the speed of the reaction of the adhesive composition. For example, it is known that certain substances, acting as inhibitors, will interfere with the catalyst in such a way as to substantially reduce the rate of polymerization, and that certain metal salts, functioning as initiators or activators, can be added to accelerate the rate of polymerization.

As used herein, the "Adhesion reaction", as illustrated in the following example wherein work pieces are bonded together, comprises two steps: initial "set-up", which is usually quick and often takes no more than a few minutes, and final "cure", which is the polymerization reaction between the acrylic-based and epoxide-based components of the adhesive. The "quick-set" feature of the present invention is obtained during this initial set-up; and the term "quick-set" as herein used means that work-pieces are substantially adhesively bonded together by the adhesive mixture of the present invention within a short period of time which may, for example, be 10 minutes or less. The bond provided by the "quick-set" is sufficient to permit some further handling of the assembled work pieces such as may be necessary for removal from an initial assembly and bonding station or apparatus prior to a final cure of the adhesive, thereby promoting faster and more economical production. Adhesive compositions of the invention provide even better bonds at elevated temperatures.

During the course of the development of the present invention, it was observed that the method of initiating the adhesion reaction was important to meet certain of the objects of the present invention. Certain aldehyde amine reaction products, acting as catalyst or

co-catalyst initiators, have proved important in obtaining the desired adhesive qualities.

In accordance with a bonding method incorporating features of the present invention, a quantity of adhesive components except for the initiating ingredient is prepared and applied to a surface of one work-piece. A quantity of the initiating material is applied to the surface of a mating work-piece and the work-pieces are then brought together. In accordance with a second bonding method of the present invention, a first work-piece has a quantity of the initiating material applied to a surface, the initiator-bearing surface of the first work-piece is then brought into close proximity to a surface of a second work-piece, with a gap between the two work-pieces, and a quantity of adhesive components (except for the initiating ingredient) is prepared and added to the gap. In accordance with a third bonding method of the present invention, a first work-piece having a surface defining a cavity has a quantity of the adhesive components (except for the initiating ingredient) prepared and added to the cavity. A second work-piece having a quantity of the initiating material applied to a surface is inserted into the cavity in a fashion such that adhesive component-covered and initiator-bearing surfaces of the respective work-pieces are positioned in close proximity. Examples of mechanical addition mechanisms for adding these adhesive components are injecting, pumping or drawing into the gap or cavity; mechanisms employing natural forces such as gravity or capillary action also illustrate bonding methods of the present invention.

When the initiator is thus separately applied, the adhesive may be termed a "no-mix" composition. The initiator functions as a "surface activator". The surface activator used herein is a substance which is

used to trigger the action of the catalyst and initiate the quick set. After the work-pieces are brought into close proximity such as to permit intimate contacting of their respective surfaces with the adhesive of the present invention, the adhesive initiates a quick set-up, generally at room temperature. Thereafter, the adhesive is caused to "cure". Clearly, since the initiator is used to trigger the action of the catalyst, a quantity of adhesive components including the initiator, but not the catalyst, can be prepared and applied to a surface of one work-piece, and a small amount of a catalytic substance can be applied to a surface of another work-piece in any of the bonding methods mentioned above.

The work-pieces may be assembled or brought together by many different means, such as through the use of rollers or clamping devices or fixtures. If desired, the work-pieces may be held by such devices during all or a portion of the quick-set period and then removed for final curing. The curing portion of the adhesion reaction may take place at room temperature or at elevated temperatures.

By way of example of the use of a "no-mix" form of the present invention, seven components are mixed together, using conventional mixing techniques, to make a storage-stable liquid mixture. In this composition, components 1 and 2 are difunctional materials, i.e. a dimethacrylate and diepoxide, respectively; component 3 is a bifunctional compound having an acrylic-based portion and an epoxide-based portion; component 4 is a bifunctional compound having an acrylic-based portion and an acidic portion which can react with an epoxide ring; component 5 provides heat-resistance and functions as a cross-linking agent, cross-linking dimethacrylate oligomers; component 6 is a polymerisation initiator; and component 7 is a co-catalyst. This mixture is applied to

one of two work-pieces, and component 8, a surface activator, to the other work-piece. When the two work-pieces are brought together, into close proximity such that the surface activator makes intimate contact with the liquid mixture, the adhesion reaction begins.

5 In such a "no-mix" adhesive composition, the methacrylate-based adhesive component provides the composite adhesive of the present invention with a quick, room temperature set, and causes partial bond strength. 10 On heating, or through passage of time, the epoxide groups react with additional components in the adhesive composition to cure fully and develop full adhesive strength.

The composite adhesive of the present invention can 15 be classified as a polymerisable mixture for adhesive bonding comprising (1) an acrylic-based adhesive component; (2) an epoxide-based adhesive component; (3) a bifunctional molecular material comprising 20 epoxide-reactive and acrylic-based reactive functional groups; and, as optional components, (4) various catalysts; (5) an activator; and (6) a cross-linking agent. The present invention combines the desirable features of acrylic-based adhesives which are 25 fast-setting, room-temperature-curing, no-mix compounds, with those of epoxide-based adhesives which are heat- and solvent-resistant and durable.

Preferably, a polymerisable composition of the invention comprises from 0.75 to 1.8 parts by weight of polymerisable acrylic-based ester component per part by 30 weight of the polymerisable epoxide-based component.

The following Examples 1 to 6, 10 and 11 illustrate the invention.

Example 1

A "no-mix" composition is prepared and used in the manner described above, using as its eight components the materials shown in Table 1.

5	<u>Compound</u>	<u>Table 1</u>		<u>Parts, By Weight</u>
		<u>Component Number</u>	<u>Type</u>	
	Ethoxylated Bisphe- nol A Dimethacrylate	(1)	dimethacrylate	35
10	Bisphenol A/ Epichlo- rohydrin Resin	(2)	diepoxide	35
	Glycidyl meth- acrylate	(3)	bifunctional	10
	Methacrylic acid	(4)	bifunctional	15
15	Trimethylolpropane trimethacrylate	(5)	crosslinker	5
	Cumene hydroperoxide	(6)	peroxide catalyst	1
20	Diphenyl ether di- sulfonyl chloride	(7)	Co-catalyst	Appx 0.2-0.5
	Amine - aldehyde Condensation product, Copper-modified	(8)	Surface activator	to cover bonding surface
25	1. Containing approximately 350 parts per million (ppm) of p-methoxyphenol as an inhibitor. 2. Containing approximately 50 ppm of p-methoxyphenol as an inhibitor. 3. Containing approximately 250 ppm of p-methoxyphenol as an inhibitor.			

30 Examples 2 to 5

Four compositions were made up, having the components shown in Table 2 (in which all parts are by weight). The heat-durability of the adhesive bonds obtained using these formulations was tested on steel which had been solvent-cleaned. One of the two steel mating surfaces had a thin film of the activator "Vanax

808" applied to it. Vanax 808 functions as an accelerator or initiator, is a mixture of butyraldehyde-aniline condensation products, and can be purchased from R. T. Vanderbilt and Company Inc. The adhesive was allowed to cure at room temperature. The adhesive bond was then subjected to a high temperature environment. The "lap shear test" (ASTM D-1002-72) was then carried out.

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Table 2

Compounds		Example			
		2	3	4	5
5	Bisphenol A/Epichlorohydrin Resin	3.5	3.0	4.0	4.5
	Ethoxylated Bisphenol A Dimethacrylate	3.5	4.0	3.0	2.5
	Glycidyl methacrylate	1	1	1	1
10	Trimethylolpropane trimethacrylate		0.5	0.5	0.5
	Methacrylic acid	1.5	1.5	1.5	1.5
	Cumene Hydroperoxide	2 drops	2 drops	2 drops	2 drops
15	Diphenyl ether disulfonyl chloride	trace	trace	trace	trace
	Lap Shear test results (kPa)				
20	Cure was 5 hours at room temperature; then bond was held at 149°C for 3 days	9650	8950	8275	7725
	Shear test performed at 149°C				
	Shear test performed at room temperature	11725	11450	11025	13800
25	Cure was 4 days at room temperature	7300	9100	11850	9375
	Then bond was held at 204°C for 1 day and tested at room temp.				
30	Then bond was held at 204°C for 3 days and tested at room temp.	8000	7725	7725	4125
35					

Examples 6 to 8

A composition was prepared comprising 37 parts bisphenol A epichlorohydrin resin, 37 parts ethoxylated bisphenol A dimethacrylate, 10 parts glycidyl methacrylate, 15 parts methacrylic acid, 0.5 parts cumene hydroperoxide and 0.1 parts diphenyl ether disulfonyl chloride (all parts are by weight).

For Example 7, a conventional acrylic adhesive was made up in the same manner, but replacing the resin with a further 37 parts of the ethoxylated bisphenol A dimethacrylate and increasing the amounts of the last two ingredients to 1 and 0.2 parts, respectively.

For Example 8, a conventional epoxy adhesive was formulated from 100 parts bisphenol A epichlorohydrin resin and 2 parts 2-ethyl-4-methylimidazole.

The adhesives were allowed to set at room temperature (approximately 25°C). The adhesives were then oven-cured for 2 hours at 70°C and subsequently for 1 hour at 177°C. Cold-rolled steel panels were used as the work-pieces. The strength of the adhesive bonds formed were tested, and the results are shown in Table 3. The bonds were tested after 1 hour, 1 week and 2 weeks at 232°C.

Table 3

Example	Lap shear test (kPa) after		
	1 hr	1 week	2 weeks
6	4950	11575	10125
7	975	1375	failed
8	1350	2750	3450

Further, high temperature chemical resistance was measured in various liquids after ageing for 1 month, either at 87°C or at room temperature. The results are in Table 4.

Table 4

		Lap shear test (kPa)		
Ageing temp. (°C)	Liquid	Ex. 6	Ex.7	Ex. 8
5 87	anti-freeze/ water (50:50)	6900	1690	4925
87	water	2975	2250	2075
87	transmiss- ion oil	11150	3025	8750
10 87	SAE 30 oil	10750	2700	8950
87	10% NaOH	1525	-	4550
25	methyl ethyl ketone	7000	1100	9250
25	(control)	7300	3300	9375

15 Examples 9 to 11

Three formulations were made, as shown in Table 5
(all parts are by weight).

Table 5

		9	10	11
20	ABS resin	2.718	1.510	0.3020
	Methyl methacrylate	5.652	3.140	0.6280
	Methacrylic acid	0.432	0.240	0.0480
25	Bisphenol A/Epichloro- hydrin Resin	1.000	5.000	9.0000
	Aliphatic amine adduct	0.200	1.000	1.8000
	Cumene Hydroperoxide	0.0432	0.024	0.0048
	Diphenyl ether 1, 1-disulfonyl chloride	0.0261	0.0145	0.0029
30	BHT antioxidant	0.0261	0.0120	0.0024
	Synthetic spermaceti wax	0.0873	0.0485	0.0097
	Vanax 808	0.1000	0.0400	0.0100

9. A method for polymerising a composition comprising a formulation as defined in claim 1 and a catalyst initiator, which comprises contacting the composition with a catalyst.
- 5 10. A method for bonding two surfaces, which comprises applying a composition comprising a formulation as defined in claim 1 and a catalyst initiator to one, and a catalyst to the other, of the surfaces, and bringing the surfaces into contact.
- 10 11. A method for bonding two surfaces, which comprises applying a catalyst initiator to one of the surfaces, bringing the surfaces into close proximity, with a gap therebetween, and introducing into the gap a composition comprising a formulation as defined in claim 1 and a
- 15 catalyst.
12. A method for obtaining a bond at a surface, which comprises applying a composition comprising a formulation as defined in claim 1 and a cross-linking agent, and subsequently a catalyst initiator, to the surface.
- 20 13. A method according to claim 12, in which the composition additionally comprises a catalyst.
14. A method for obtaining a bond at a surface, which comprises applying a composition comprising a formulation as defined in claim 1 and a cross-linking agent, and
- 25 subsequently a catalyst, to the surface.
15. A method for obtaining a bond at a surface, which comprises applying a catalyst, and subsequently a composition comprising a formulation as defined in claim 1 and a cross-linking agent, to the surface.
- 30 16. A method according to claim 14 or claim 15, in which the composition additionally comprises a catalyst initiator.
17. A method according to any of claims 12 to 16, which is conducted at ambient temperature.
- 35 18. A method according to claim 17, which comprises the additional step of curing at an elevated temperature.
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CLAIMS

1. A polymerisable composition which comprises a formulation of 1 part by weight of a polymerisable epoxide-based material; no more than 1.8 parts by weight
5 of a polymerisable acrylic-based material; and a bifunctional compound; in which the polymerisable materials are mutually substantially non-reactive at ambient temperature, and in which the bifunctional compound can react with both polymerisable materials at
10 ambient temperature; and in which the composition additionally comprises a catalyst and a catalyst initiator.
2. A composition according to claim 1, wherein the polymerisable acrylic-based material is methyl
15 methacrylate.
3. A composition according to claim 1 or claim 2, wherein the polymerisable epoxide-based material is bisphenol A epichlorohydrin or the diglycidyl ether of bisphenol A.
- 20 4. A composition according to any preceding claim, wherein the bifunctional compound is glycidyl methacrylate or methacrylic acid.
5. A composition according to any preceding claim, which comprises from 0.75 to 1.8 parts by weight of a
25 polymerisable acrylic-based ester material per part by weight of the polymerisable epoxide-based material.
6. A composition according to any preceding claim, which additionally comprises a cross-linking agent.
7. A composition according to claim 1, substantially as
30 described in Example 10 or Example 11.
8. A method for polymerising a composition comprising a formulation as defined in claim 1 and a catalyst, which comprises contacting the composition with a catalyst initiator.

Table 6

	Lap shear test results, (kPa)	Example	9	10	11
5	Cured at	30 minutes	n.t.	1375	n.t.
	elevated temperatures for	24 hours	10275	17000	13625
	Peel strength test results (kg/m)	Example	9	10	11
10	Cured for:	2 days at room temperature.	2075	1850	1150
		2 hours at 65°C	0	2200	0

In addition to the specific bonding examples presented above, the composite adhesive of the present invention can be used in many commercial or industrial applications. For example, the adhesive of the present invention can be used to bond a steel motor magnet to an aluminium housing; and it can be used to adhesively bond a variety of plastics work-pieces together. In the construction area, the present invention can be used to adhesively bond reinforcing members, thereby eliminating the need to use conventional welding or other fastening techniques. In addition, the composite adhesive of the present invention can be used to bond surfaces which are not necessarily clean.

In these formulations, ABS (acrylonitrile-butadiene-styrene) resin was added to the mixture to make the adhesive more viscous and the cured bond more flexible. Increased viscosity often enhances the quick-set feature of an adhesive. An aliphatic amine adduct, a known curing agent for epoxy resins, was included in the mixture. A butylated hydroxytoluene (BHT) anti-oxidant ingredient, a known stabiliser, was added to the mixture to counteract the effect of the hydroperoxide ingredient, and give the adhesive mixture a longer shelf-life. The aliphatic amine adduct, an optional ingredient, is also known to retard the cure under certain conditions. A synthetic spermaceti wax, another optional ingredient, tends to migrate to the surface of the adhesive mixture, and thereby prevents the volatile components from evaporating, if such is desired. The components were mixed in the weight proportions indicated. The adhesive was then applied to etched aluminium strips for adhesive testing.

Bonds produced using the formulations of these Examples were tested for lap shear strength and high peel strength (test results obtained performing ASTM D-1876-61T) while, at the same time, quickly bonding together the work-pieces because of the quick set and rapid cure rate. The results are shown in Table 6.